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Thermodynamic calculations for liquid alloys with an application to sodium–caesium

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Abstract. A semi-empirical model is presented for the analysis in liquid alloys of the long wavelength limit of the structure factor, the free energy of mixing and the electrochemical potential. The formalism is partly based on statistical mechanics assuming a concentration-dependent hard-sphere behaviour of liquid alloys. Although being conceptually quite different, our description incorporates the Flory–Huggins model as a first approximation.

1. Introduction

The sodium–caesium liquid alloys form a typical example of a binary system to which regular solution theory is not applicable. The main reason for this is that the ratio of the atomic volumes is as large as three which precludes any interpretation in terms of a simple lattice model (Guggenheim 1952). In the past, such systems have been described with fair success by the Flory–Huggins theory (Flory 1942, Huggins 1942). It is based upon a lattice model originally developed for polymers, but could be extended to a more general class of mixtures. This theory provides approximate relations for the heat of mixing and the entropy. From the free energy thus obtained, several thermostatistical quantities, like activities and number density fluctuations, can be derived (Bhatia and March 1975). Although the Flory–Huggins theory offers a nice general framework for interpretation of thermodynamic data, it suffers from quantitative inconsistencies (Huyben 1978).

The alternative method proposed in this paper is a semi-empirical one: the energy term is essentially taken from experiment, the entropy is derived from a hard-sphere model for the liquid state. It will be shown that the entropy, derived in this way, contains the Flory–Huggins entropy term as a first approximation. The method is rather general and may be applied to a large number of binary mixtures, metallic or non-metallic. As a numerical example we report details of an investigation on sodium–caesium liquid alloys.

This system was chosen because its structure and its thermodynamic properties have been rather well scrutinised. In order to obtain the small-angle limit of the structure factor, $S(0)$, Huyben (1978) and Huyben *et al* (1979) performed x-ray and

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neutron diffraction studies of sodium–caesium alloys. Chemical activities of sodium–caesium alloys were determined by Ichikawa *et al* (1974) while Yokokawa and Kleppa (1964) measured the enthalpy of mixing. The densities were determined by Huyben *et al* (1975).

One of the parameters involved in almost any theory of binary mixtures is the interchange energy w, often quoted as the reduced quantity $W = w/kT$. Within the framework of the Flory–Huggins model, three different values for the interchange energy parameter W are found depending on which experiment was taken to be fitted. In figure 1 the structure factors in the small-angle limit, $S(0)$, are depicted as a function of composition. They are calculated using the following values of W: 0·77, 1·04 and 1·14, obtained by fitting to the enthalpy of mixing, the structure factor, and the activity data, respectively. Figure 2 shows the striking discrepancies between the values of the enthalpy of mixing, calculated with the Flory–Huggins model, using $W = 1{\cdot}14$, and the experimental values.

In the following section we describe the limited applicability of the Flory–Huggins model in the case of NaCs alloys and give an outline of our model. In §3 we present the computational procedure and the results. Finally, the subsequent §4 contains a discussion on the limitations of the proposed model and concluding remarks.

2. Calculation of the free energy of mixing

2.1. The Flory–Huggins model

All the thermodynamic quantities in this paper are expressed in the appropriate units

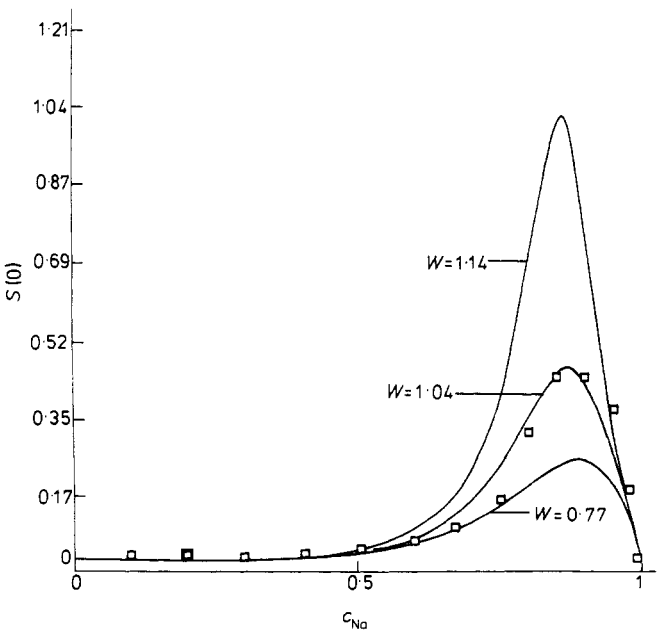

Figure 1. The long-wavelength limit of the x-ray structure factor $S(0)$ calculated as a function of the sodium concentration in NaCs alloys using different values for the interchange energy W (□: experiment).

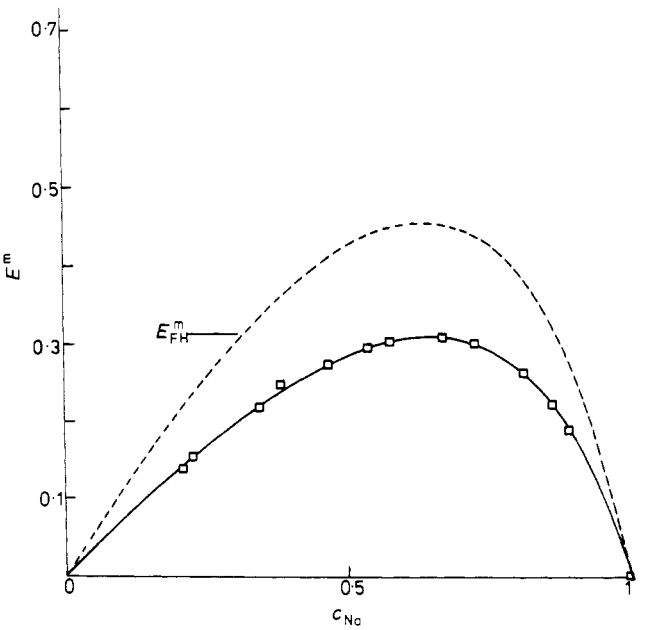

Figure 2. The energy of mixing (in units of kT) calculated as a function of the sodium concentration in NaCs alloys using two different expressions for the interchange energy W: $W_{FH} = 1{\cdot}14$ and $W = 0{\cdot}7106 + 0{\cdot}1086\, c_{Na}$. E^m_{FH} refers to the Flory–Huggin energy of mixing and the points indicate the experimental values.

per particle. As has been illustrated in figures 1 and 2 of the preceding section, the Flory–Huggins model is not able to describe satisfactorily both the long-wavelength limit of the structure factor and the heat of mixing of liquid NaCs alloys. If the ratio of the atomic volumes of the two components is represented by $\gamma(\gamma_{NaCs} = 2{\cdot}987$ (Huyben *et al* 1975)), the free energy of mixing in the Flory–Huggins model (indicated by subscript FH) is given by:

$$F^m_{FH} = kT(E^m_{FH}/kT - S^m_{FH}/k) \tag{1}$$

where

$$E^m_{FH}/kT = W\, c_1\gamma(1 - c_1)/[c_1 + \gamma(1 - c_1)] \tag{2}$$

represents the Flory–Huggins energy of mixing and

$$\frac{S^m_{FH}}{k} = -c_1 \ln\left(\frac{c_1}{c_1 + \gamma(1 - c_1)}\right) - (1 - c_1)\ln\left(\frac{(1 - c_1)\gamma}{c_1 + \gamma(1 - c_1)}\right) \tag{3}$$

is the entropy of mixing. c_1 is the atomic fraction of the component with the smallest atomic volume. Bearing in mind that the Flory–Huggins model incorporates serious simplifications and is not particularly developed for metallic systems, one can only expect qualitative agreement between experiment and computational results. If the free energy of mixing can be calculated using a value of $W = 1{\cdot}14$, the heat of mixing ΔE^m appears to be 30% too high as depicted in figure 2. Obviously, although the Flory–Huggins model can be fitted nicely to each of the individual experiments, inconsistencies arise when a complete and uniform description of the NaCs system is required.

2.2. An alternative approach

In order to calculate the free energy of mixing we have chosen a semi-empirical approach, deriving the energy term from the experimental heat of mixing and the entropy from an existing theory of the liquid state. This is not inconsistent, because the entropy is determined by the volume in configuration space and is to a high degree independent of the interatomic interactions. So, in contrast to the energy term, the entropy term may be quite well represented by a hard-sphere model.

For the energy we have made an analytical fit to the observed values of the heat of mixing given by Yokokawa and Kleppa (1964) to obtain a concentration-dependent energy term in the free energy of mixing.

The entropy term in our approach is based on a hard-sphere description of liquid systems given by Mansoori *et al* (1971). We have adopted the following formulae from a paper by Umar *et al* (1976).

$$S_{hs} = S_{gas} + S_c + S_\eta + S_\sigma \tag{4}$$

where

$$\frac{S_{gas}}{k} = \ln\left[\Omega\left(\frac{m_1^{\,c_1} m_2^{\,c_2} kT}{2\pi\hbar^2}\right)^{3/2}\right] + \frac{5}{2} \tag{5}$$

$$S_c/k = -(c_1 \ln c_1 + c_2 \ln c_2) \tag{6}$$

$$S_\eta/k = -(\zeta - 1)(\zeta + 3) \tag{7}$$

$$S_\sigma/k = \tfrac{3}{2}(\zeta^2 - 1)Y_1 + \tfrac{3}{2}(\zeta - 1)^2 Y_2 - (Y_1 + Y_2)\{[\tfrac{1}{2}(\zeta - 1)(\zeta - 3)] + \ln \zeta\}. \tag{8}$$

Here $\zeta = (1 - \eta)^{-1}$, $\eta = \pi(c_1\sigma_1^3 + c_2\sigma_2^3)/6\Omega$ is the packing fraction and Ω is the volume per particle. m_i are in units of the electronic mass and c_1 is the atomic concentration of component 1, (sodium):

$$c_1 = N_1/N \tag{9}$$

N_1 being the number of sodium atoms in the mixture and N representing the total number of particles.

S_{gas} represents the ideal gas entropy, S_c is the ideal entropy of mixing and S_η depends only on the packing density η. The last term in equation (4) corresponds to the mismatch between hard spheres with different diameters σ.

In equation (8)

$$Y_1 = c_1 c_2(\sigma_1 + \sigma_2)(\sigma_1 - \sigma_2)^2(c_1\sigma_1^3 + c_2\sigma_2^3)^{-1} \tag{10}$$

and

$$Y_2 = c_1 c_2(\sigma_1 - \sigma_2)^2\sigma_1\sigma_2(c_1\sigma_1^2 + c_2\sigma_2^2)(c_1\sigma_1^3 + c_2\sigma_2^3)^{-2} \tag{11}$$

where σ_1 and σ_2 are the effective hard-sphere diameters of Na and Cs, respectively.

In the hard-sphere model the entropy of mixing per particle is given by:

$$S_{hs}^m = S_{hs} - c_1 S_{hs}^{(1)} - c_2 S_{hs}^{(2)} \tag{12}$$

where

$$S_{hs}^{(i)} = S_{gas}^{(i)} + S_\eta^{(i)} \tag{13}$$

$$S_{gas}^{(i)}/k = \ln[\Omega_i(m_i kT/2\pi\hbar^2)^{3/2}] + \tfrac{5}{2} \tag{14}$$

$$S_\eta^{(i)}/k = -(\zeta_i - 1)(\zeta_i + 3). \tag{15}$$

Here, η_i is equal to $\pi\sigma_i^3/6\Omega_i$. If c_1 is equal to one or equal to zero, Y_1, Y_2 and S_c are equal to zero. Substitution of equations (4), (13), (14), (15) into equation (12) yields:

$$S_{hs}^m = \Delta S_{gas} + S_c + \Delta S_\eta + S_\sigma \tag{16}$$

where

$$\Delta S_{gas} = S_{gas} - c_1 S_{gas}^{(1)} - c_2 S_{gas}^{(2)} \tag{17}$$

and

$$\Delta S_\eta = S_\eta - c_1 S_\eta^{(1)} - c_2 S_\eta^{(2)}. \tag{18}$$

Using equation (16) and the relation between η and the σ_i we are able to express the entropy of mixing depending on the variables c_1, c_2 and the parameters σ_1, σ_2, Ω_1, Ω_2 and Ω. Since experimental information about the volumes exists we are left with only three independent parameters in equation (16): σ_1, σ_2 and c_1. It turned out that a small composition dependence of σ_i has to be admitted for an optimum reproduction of the experiments. This variation of the σ_i allows for the inherent deficiencies of a hard-sphere description in the whole range of composition. The temperature is taken to be constant at 383 K.

It is noteworthy that after adding $\Delta S_{gas}/k$ to S_c/k we obtain:

$$-c_1 \ln\left(\frac{c_1}{c_1 + \gamma(1 - c_1)}\right) - (1 - c_1)\ln\left(\frac{\gamma(1 - c_1)}{c_1 + \gamma(1 - c_1)}\right) + \ln\left(\frac{\Omega}{\Omega_{ideal}}\right) \tag{18}$$

where $\gamma = \Omega_2/\Omega_1$ and $\Omega_{ideal} = c_1\Omega_1 + c_2\Omega_2$ represents the volume per particle in an ideal solution. If we compare equation (18) and equation (16) with equation (3) we conclude that the entropy of mixing resulting from a hard-sphere model still contains the Flory–Huggins description of the entropy of mixing. Although the latter formalism is completely different from the hard-sphere model, equation (18) gives an explanation for the fact that the Flory–Huggins theory can provide at least a qualitative description of a liquid binary alloy.

Substituting equation (3) into equation (16) the entropy of mixing can be written as:

$$S_{hs}^m = S_{FH}^m + S_\Omega + \Delta S_\eta + S_\sigma \tag{19}$$

where $S_\Omega = k \ln(\Omega/\Omega_{ideal})$.

From equation (19) we can state in conclusion that the hard-sphere model actually provides three corrections to the Flory–Huggins entropy of mixing which are due to:

(i) the excess volume of the alloy ($\ln(\Omega/\Omega_{ideal})$);

(ii) the spherical shape of the ions and their corresponding diameters; and consequently

(iii) the slight concentration dependence of the hard-sphere diameters.

Anticipating the final calculations, in figure 3 the separate terms of equation (19) which contribute to the entropy of mixing are depicted. Evidently S_σ and ΔS_η are approximately nullifying each other as contributions to the entropy of mixing. Nevertheless, these two terms are important when calculating the $S(0)$, as in this quantity the second derivative of the free energy with respect to the composition is involved.

Assuming that the entropy of the conduction electrons remains unchanged upon transferring from the pure state to the solution, we approximate the energy of mixing

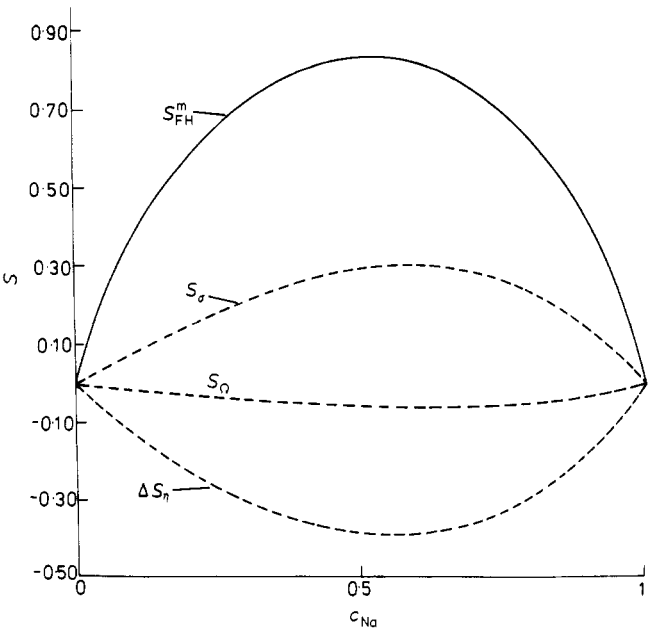

Figure 3. The separate terms which contribute to the entropy of mixing per particle (in units of k) as a function of c_{Na}, S_σ, ΔS_η and S_Ω are defined in the text.

of NaCs alloys by:

$$F^m(c_1, \sigma_1, \sigma_2) = E^m_{exp}(c) - kT\, S^m_{hs}(c_1, \sigma_1, \sigma_2) \tag{20}$$

(where T is constant).

3. Computational procedure and results

The first step in the elaboration of equations (19) and (20) is the construction of a third-order polynomial function which describes the experimentally observed excess volumes of liquid NaCs alloys at 373 K by Huyben *et al* (1975). The observed values of the excess volumes $\Delta\Omega$ as well as our fit are shown in figure 4, where

$$\Delta\Omega = (\Omega - \Omega_{ideal})/\Omega_{ideal}. \tag{21}$$

Since S_Ω, ΔS_η and S_σ depend on Ω, the excess volume $\Delta\Omega$ has great influence on the corrections of the Flory–Huggins entropy of mixing introduced by the hard-sphere model. This is particularly so in the case of NaCs, where the volume contraction on mixing is appreciable (5·6%).

Secondly, the experimental heat of mixing had to be expressed in an analytical form. We have shown that the Flory–Huggins theory describes the data with reasonable accuracy when a simple, suitably chosen, value of W is substituted in equation (2). For further optimisation, W was written as a linear function of c_1:

$$W = 0{\cdot}7106 + 0{\cdot}1086\, c_1 \tag{22}$$

which, after substitution in equation (2), resulted in a close fit to E^m (figure 2).

In the literature a considerable scatter exists in the hard-sphere diameters and

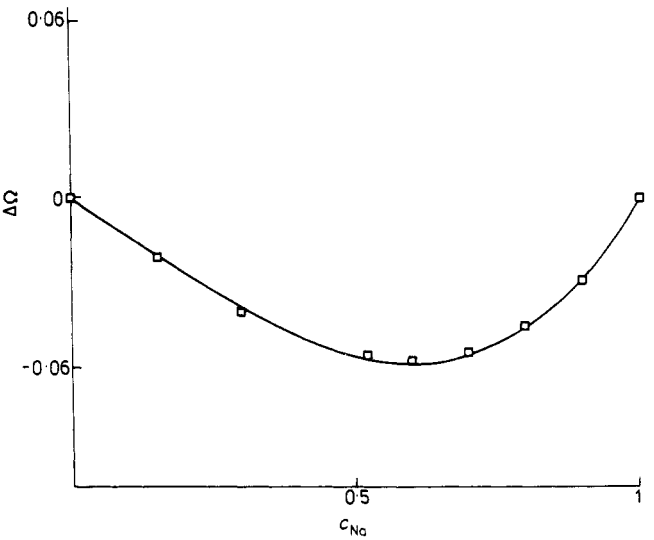

Figure 4. The excess volume $\Delta\Omega$ in NaCs alloy as a function of c_{Na} (□ : experiment). $\Delta\Omega$ is defined in the text.

packing fractions of the pure liquids Na and Cs. These data are compiled in table 1. In our calculations we imposed only restrictions on the values of the diameters of the pure components. Rather arbitrarily these values are not permitted to deviate more than five per cent from the mean values of those listed in table 1: 6·26 au and 9·071 au, respectively.

The free energy of mixing was calculated using equation (20) and compared with the results obtained for F^{m}_{FH} based on the Flory–Huggins model with $W = 1{\cdot}14$. From the free energy of mixing calculated, the mean-square fluctuations in the concentration in the long-wavelength limit $N^{-1}S_{CC}(0)$ (Bhatia and Thornton 1970) can be obtained according to the following equation:

$$N^{-1}S_{CC}(0) = kT\left(\frac{\delta^2 F^{m}}{\delta c_1^2}\right)^{-1}_{N,P,T}. \tag{23}$$

Table 1. The hard-sphere diameters and packing fraction as function of the concentration of sodium in NaCs alloys (in au).

c_1	σ_1	σ_2	η
1	6·468[1]	—	0·490[1]
	6·230[2]	—	0·450[2]
	6·087[3]	—	0·421[3]
0·5	5·95[4]	9·12[4]	0·466[4]
0	—	9·003[1]	0·460[1]
		9·140[2]	0·480[2]

[1] Huyben (1978).
[2] Kumaravadivel and Evans (1976).
[3] Umar *et al* (1974).
[4] Hafner (1977).

$S_{CC}(0)$ in turn is related to the long-wavelength limit of the x-ray structure factor $S(0)$ by:

$$S(0) = \frac{\langle f \rangle^2}{\langle f^2 \rangle}\left[\left(\delta - \frac{f_1 - f_2}{\langle f \rangle}\right)^2 S_{CC}(0) + \rho_0 \chi_T kT\right] \tag{24}$$

where $\langle f \rangle = c_1 f_1 + c_2 f_2$, f_i is the long-wavelength limit of the atomic scattering factor, χ_T represents the isothermal compressibility, ρ_0 is the particle density (Huyben 1978), and:

$$\delta = \frac{1}{\Omega}\left(\frac{\delta\Omega}{\delta c_1}\right)_{N,T,P}. \tag{25}$$

In this way, using equations (23) and (24) the computed free energy of mixing is also related to $S(0)$ which can be compared with experimentally determined $S(0)$ (Huyben *et al* 1979). We may remark here that, as two differentiations with respect to c_1 are involved in deriving $S_{CC}(0)$ from the free energy, the $S_{CC}(0)$ are extremely sensitive to small deviations of F^m and that, consequently, F^m has to be determined very accurately. It is mainly for this reason that a small c-dependence of the σ_i has to be introduced.

It was presumed that the concentration-dependent diameters σ_1, σ_2 could be described using a third-order polynomial function of the concentration c_1. Applying an iteration procedure we have optimised the coefficients appearing in the polynomials so that the deviations between the calculated and observed values of F^m and of $S(0)$ are minimal (still keeping $W = 1{\cdot}14$). The second derivative of F^m with respect to c_1 was determined analytically instead of numerically to avoid appreciable errors. Moreover,

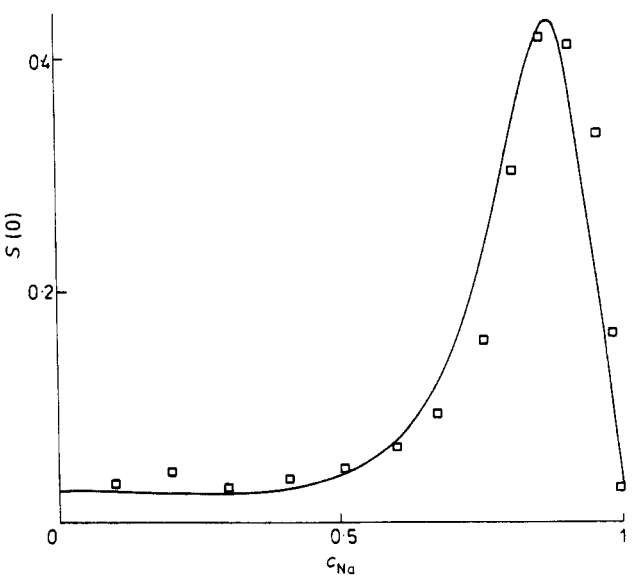

Figure 5. Best fit to the measured long-wavelength limit of the structure factor $S(0)$ as a function of c_{Na} calculated according to the method proposed in this paper. (□: experiment.)

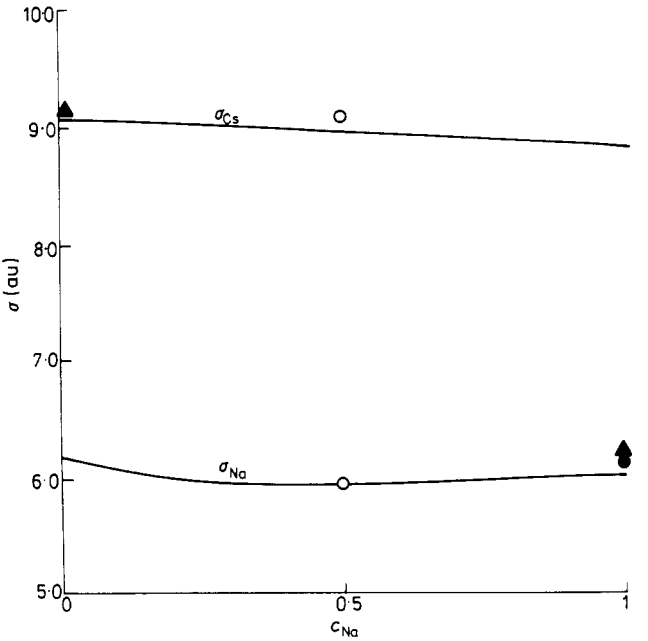

Figure 6. The hard-sphere diameters of Na (σ_1) and Cs (σ_2) as function of c_{Na} (○: Hafner (1977), ●: Umar *et al* (1974), ▲: Kumaravadivel and Evans (1976)).

in evaluating $S(0)$ we approximated the last term in equation (24) by a linear interpolation of the known values of the pure components. Through that, however, we make only a negligible error in S(0) since in the most interesting composition range, near the peak of $S_{CC}(0)$, the compressibility term in equation (24) is much smaller than the term containing $S_{CC}(0)$.

The best fit to the measured structure factor $S(0)$ as a function of the concentration c_{Na} is shown in figure 5. The polynomial functions are given by:

$$\sigma_1 = 6{\cdot}184 - 1{\cdot}302\, c_1 + 2{\cdot}138\, c_1^2 - c_1^3 \tag{26}$$

$$\sigma_2 = 9{\cdot}079 - 0{\cdot}257\, c_1 + 0{\cdot}005\, c_1^2 + 0{\cdot}006\, c_1^3 \tag{27}$$

(in au) and are depicted in figure 6.

Another observed experimental property is the electrochemical potential E measured by Ichikawa *et al* (1974):

$$E = -N_{av}\Delta\mu_1/F^1 \tag{28}$$

which is related to the free energy of mixing through the change of the chemical potential $\Delta\mu_1$ of Na on alloying:

$$\Delta\mu_1 = F^m + (1 - c_1)\left(\frac{\delta F_m}{\delta c_1}\right)_{N,T,P} \tag{29}$$

where F^1 represents the Faraday constant. Using equation (28) and the free energy of mixing calculated we are able to predict the activity data. Both the results of this concentration-dependent hard-sphere model and those obtained using the Flory–Huggins model (Bhatia and March 1975) are plotted in figure 7.

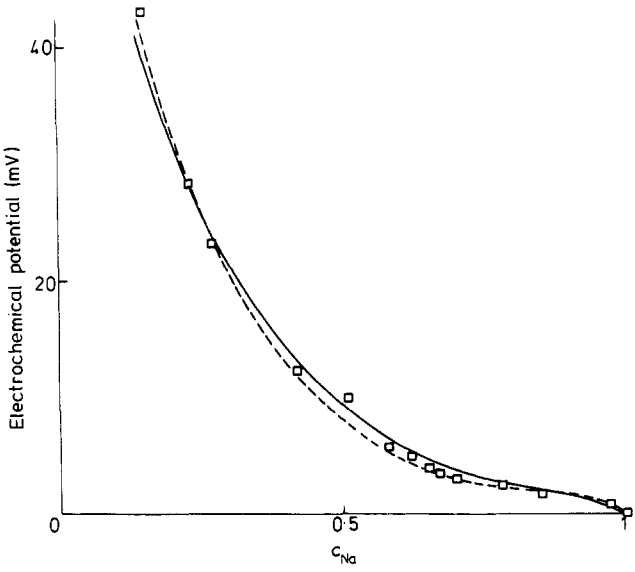

Figure 7. Electrochemical potential of NaCs alloy as a function of c_{Na}. The full curve indicates the results obtained using the method presented in this paper; and the broken curve refers to the results based on the Flory–Huggins model applied by Bhatia and March (1975) ($W = 1{\cdot}14$).

4. Discussion and conclusions

Our main conclusion is that the model of Mansoori *et al* provides a fair approximation to the entropy of liquid NaCs alloys and leads to a consistent description of various thermodynamics properties. Furthermore, we found that both the height and

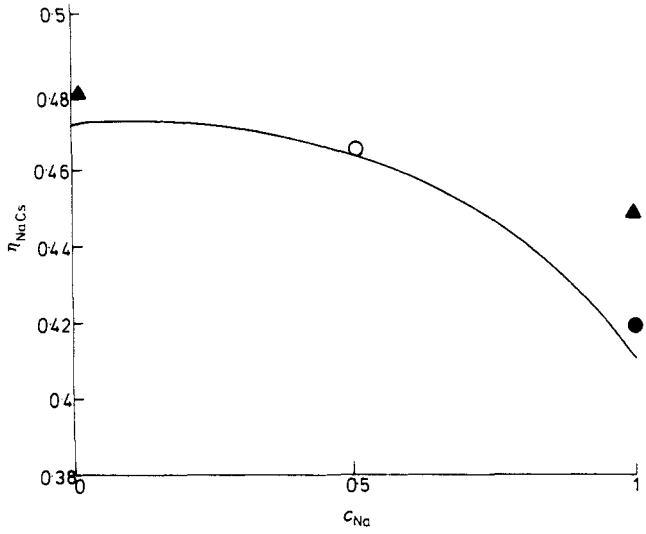

Figure 8. The packing fraction of the NaCs mixture as a function of c_{Na} (○: Hafner (1977), ●: Umar *et al* (1974), ▲: Kumaravadivel and Evans (1976)).

the position of the long-wavelength limit of the structure factor $S(0)$ as a function of the concentration c_1 are extremely sensitive to the choice of the hard-sphere diameters. In contradistinction, the activity of sodium is far less sensitive to those diameters. In fact, these diameters can be determined accurately only if an observed peaking of the long-wavelength limit of the structure factor exists at a certain concentration. When contemplating such details, it should be remembered that the computational procedure depends upon the accuracy of the experimentally observed energy of mixing and volume concentration.

The packing fractions of the mixture are calculated and plotted in figure 8 as function of c_{Na}. From figure 6 and figure 8 we may state in conclusion that:

(i) the variation of σ_1 and σ_2 as a function of c_{Na} is about 3 per cent;
(ii) $\sigma_1 = 6{\cdot}019$ au in pure sodium and $\sigma_2 = 9{\cdot}079$ au in pure caesium;
(iii) the packing fraction η varies from 0·472 (pure caesium) to 0·410 (pure sodium).

The diameter and packing fraction calculated are in reasonable accordance with the results obtained by Hafner (1977), Umar *et al* (1974) and Kumaravadivel and Evans (1976), suggesting that there is an encouraging consistency in the choice of optimum parameters for the calculation of a variety of physical properties.

A stringent test for our alternative approach is of course the calculation of the change in entropy on alloying. The selected values σ_1 and σ_2 are backed by the reference to the experimental excess entropies $S^E(\equiv S_\eta)$ for the pure metals sodium and caesium, respectively (Ichikawa *et al* 1974): $-3{\cdot}45$ (calculated $-3{\cdot}26$) and $-3{\cdot}56$ (calculated $-4{\cdot}37$). From figure 3 it follows that the value for the entropy of mixing of $Na_{50}Cs_{50}$ is $\Delta S^m = 1{\cdot}35\,\text{cal}\,g^{-1}$ atom K, which is in good agreement with the experimental value $\Delta S^m = 1{\cdot}20\,\text{cal}\,g^{-1}$ atom K measured by Ichikawa *et al* (1974). As far as the experimental results are available, the agreement with our approach is as good as can be expected.

Analytically we have found that one may consider the hard-sphere model used here as a formalism providing various corrections on the lattice model proposed by Flory and Huggins. It predicts a twenty per cent lower entropy of mixing than does the Flory–Huggins theory. As a consequence, the interchange energy W must be about twenty per cent too high when the Flory–Huggins model is fitted to activity data. It is in fact thirty per cent too high and this result bears out the correctness of our prediction. Actually, fitting to activity data introduces an 'entropy part' into this energy term of the Flory–Huggins model. According to Guggenheim (1952) and Bawn (1948) the interchange energy W should be regarded as an empirical constant.

Comparing the Flory–Huggins model and the approach presented here, the Flory–Huggins model has the advantage of its elegance by giving, from elementary statistical considerations, expressions for the entropy as well as the energy, whereas the description presented here is quantitatively more consistent, makes better use of existing experimental data and provides an interesting check on the Mansoori–Carnahan–Starling–Leland approach to the entropy of a binary liquid system.

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